Melting Point Gram-Atomic Volumes and Enthalpies of Atomization for Liquid Elements

by

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"This work was done with support from the U.S. Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of the Lawrence Berkeley Laboratory nor of the U. S. Energy Research and Development Administration."

Values of the gram-atomic volumes and enthalpies of atomization to the monatomic ideal gas state for liquid elements at their melting points have been collected to facilitate predictions of the behavior of mixed systems. Estimated values are given for experimentally undetermined quantities.

Values of ΔH°_o for the atomization of elements at 0 K were taken from the compilation of Brewer.[1] Heat contents and heats of fusion from various sources were used to derive the enthalpies of atomization of the liquid elements at their melting points. The appropriate relation is

$$\Delta H^\circ_{T_m} = \Delta H^\circ_o - (H_{T_m}-H_o)_{solid} - \Delta H_f + (H_{T_m}-H_o)_{monatomic\ ideal\ gas},$$

where ΔH_f is the heat of fusion at the normal melting point. Where noted, the triple point or boiling point has been used rather than the melting point.

Volumes have been estimated as explained in the Appendix. Volumes of solids at room temperature calculated from metallic radii were multiplied by factors derived from analogous elements to take into account thermal expansion and phase changes. Solid volumes used as references are from Donohue.[2]

Experimental determination of the volumes of actinides beyond Bk are absent or subject to great uncertainty. The crystallographic data for Cf[3], which has been used to predict divalency for Cf and Es[3,4] has been shown to be that of a compound rather than Cf metal.[5] In accordance with Brewer[1] the metals Cf, Es, Fm, and Lr have been treated as trivalent, and Md and No as divalent. Melting points, heats of fusion, and volumes have been accordingly estimated after the pattern of divalent and trivalent lanthanides.

In Table I, melting points are referred to the 1968 International Practical Temperature Scale. Values are given for ΔH°_{gd}, the enthalpy of atomization to the monatomic ideal gas in the electronic ground state, and for ΔH°_{val}, the enthalpy of atomization to the gas in the valence state with the same electronic configuration as in the liquid state. The procedures for the calculation of ΔH°_{val} can be found in Reference 1.

Table I
Melting Point Gram-Atomic Volumes and Enthalpies of Atomization for Liquid Elements

Element	T_m,K	Ref.	V_ℓ,cm^3/g.a.	Ref.	ΔH_f,cal/g.a.	Ref.	ΔH°_{gd},cal/g.a.	ΔH°_{val},cal/g.a.	Ref.	Valence State	Notes
Ac	1324	6	(27.4)		(3400)	9	(88 300)	(133 300)	9	$d^{0.5}sp^{1.5}$	a
Ag	1235.08	6	11.56	16	2650	23	63 784	(196 780)	6	$d^{8.5}sp^{1.5}$	
Al	933.52	6	11.29	16	2580	6	74 994	157 994	6	sp^2	
Am	1449	7	(19.0)		(2900)		(57 500)	(143 500)		f^6dsp	a
Ar	83.81	6	27.88	17	284	6	1577		6	s^2p^6	
As	1089	8	14.35	16	6000	4	66 850		9	s^2p^3	b,c
At	(575)	9	(36)		(2850)	9	(18 587)		9	s^2p^5	a
Au	1337.58	6	11.36	16	3060	23	83 159	(223 200)	6	$d^{8.5}sp^{1.5}$	
B	2365	10	5.20	16	12 000	6	119 536	(201 540)	6	sp^2	
Ba	1002	6	41.47	16	1852	6	38 492	68 992	6	$d^{0.5}sp^{0.5}$	
Be	1562	6	5.33	16	(2919)	6	72 334	(134 830)	6	sp	
Bi	544.592	6	20.83	16	2700	6	47 023		6	s^2p^3	
Bk	1562		(18.0)		(3300)		(62 300)	(128 300)		f^8dsp	a
Br	265.9	6	24.87	18	1263.5	6	26 573		6	s^2p^5	
C	(4765)	11	(7.46)	11	(30 000)	11	(137 100)	(233 620)	11	sp^3	b,d
Ca	1113	6	29.69	16	2040	6	38 036	88 736	6	$d^{0.5}sp^{0.5}$	
Cd	594.258	6	14.06	16	1480	6	24 750	110 820	6	sp	
Ce	1072	6	20.95	16	1305	6	96 825	135 125	6	$fdsp$	
Cf	(1700)		(18.0)		(3300)		(34 300)	(128 300)		f^9dsp	a
Cl	172.18	6	20.78	18	765.5	6	31 321		6	s^2p^5	b

cont'd.

Table I, contd.

Cm	1613	12	(18.9)		3310	12	(83 500)	(127 500)		f^7dsp	a
Co	1770	6	7.61	16	3640	23	94 341	(187 140)	6	$d^{6.5}sp$	
Cr	2133	6	8.28	16	(4047)	6	84 498		6		
Cs	301.54	6	72.36	16	500	6	17 671		6	s	
Cu	1357.6	6	7.91	16	3131	23	75 751	(191 350)	6	$d^{8.5}sp^{1.5}$	
Dy	1684	6	(20.75)		2643	6	61 882	(127 680)	6	f^9dsp	a
Er	1797	6	(21.00)		4757	6	66 403	132 100	6	$f^{11}dsp$	a
Es	(1700)		(18.0)		(3300)		(30 500)	(133 500)		$f^{10}dsp$	a
Eu	1091	6	(32.84)		2202	6	38 017	76 620	6	$d^{0.5}sp^{0.5}$	a
F	53.48	6	11.14	19	61.0	6	19 264		6	s^2p^5	b
Fe	1811	6	7.94	16	3370	23	90 265		6		
Fm	(1800)		(16.9)		(3300)		(28 500)	(135 500)		$f^{11}dsp$	a
Fr	(300)	9	(82.1)		(500)	9	17 495		9	s	a
Ga	302.89	6	11.82	16	1336	6	63 663	172 260	6	sp^2	
Gd	1587	6	(20.88)		2403		89 738	129 840	6	f^7dsp	a
Ge	1211.4	6	13.23	16	8830	6	81 041		6	sp^3	
$H_{(eq)}$	13.810	6			14.025	6	51 776		6	s	b
He	4.215		32				20		6	s^2	a,e
Hf	2504	6	(14.87)	16	(5750)	6	138 084	(178 000)	6	$d^{2.5}sp^{0.5}$	
Hg	234.288	6	14.66	16	548.6	6	14 796	122 370	6	sp	
Ho	1745	6	(21.04)		(2911)	6	63 292	(130 792)	6	$f^{10}dsp$	a
I	386.7	6	31.88	18	1870	6	23 474		6	s^2p^5	
In	429.784	6	16.37	16	780	6	56 995	156 995	6	sp^2	
Ir	2720	6	(9.61)	16	(6247)	6	149 868	(268 770)	6	$d^{6.5}sp^{1.5}$	

cont'd.

Table I, contd.

K	336.34	6	47.18	16	588	6	20 682		6	s	
Kr	115.77	6	34.17	17	391.5	6	2209		6	s^2p^6	b
La	1194	6	23.35	16	1481	6	100 249	123 050	6	$d^{1.5}sp^{0.5}$	
Li	453.7	6	13.47	16	717	6	37 158		6	s	
Lr	(1900)		(16.1)				(65 000)	(144 000)		$f^{14}dsp$	a
Lu	1938	6	(19.62)		(4457)		94 391	144 190	6	$f^{13}dsp$	a
Md	(1100)		(25.5)		(2000)		(22 900)	(79 900)		$f^{13}sp$	a
Mg	922	6	15.30	16	2026	6	31 833	94 330	6	sp	f
Mn	1520	6	9.55	16	(2882)	6	58 957	109 660	6	$d^{5.5}sp^{0.5}$	
Mo	2895	6	(10.26)	16	8930	23	140 781		6	d^5s	
N	63.148	6	15.97	19	86.15	6	113 250		6	s^2p^3	b
Na	371.0	6	24.17	16	621	6	24 826		6	s	
Nb	2750	13	(11.87)	16	8260	23	164 594		6	d^4s	
Nd	1290	6	21.57	16	1707	6	73 599	131 600	6	f^3dsp	
Ne	24.555	6	16.76	19	79.28	6	449.6		6	s^2p^6	b
Ni	1728	6	7.44	16	4110	23	95 755	(192 360)	6	$d^{7.5}sp^{1.5}$	
No	(1100)		(24)				(21 900)	(81 900)		$f^{14}sp$	a
Np	910	6	(14.2)		(1400)		(99 000)	(167 000)		f^3d^3s	a
O	54.361	6	12.24	19	53.2	6	59 910		6	s^2p^4	b
Os	3306	6	(9.46)	16	(7950)	6	178 860	245 960	6	d^6sp	
P(w)	317.3	6	17.7		157	6	75 448		6	s^2p^3	
P(r)	862.8	6	27.0	20						s^2p^3	b,g
Pa	1848	14	(21.0)		(3500)	9	(135 000)	(155 000)	9	fd^3s	a
Pb	600.652	6	19.57	16	1147	6	44 959		6	s^2p^2	

cont'd.

Table I, contd.

Pd	1827	6	10.14	16	4050	23	83 447	223 650	6	$d^{7.5}sp^{1.5}$	
Pm	(1300)	9	(21.6)		(3000)	9	(69 300)	(131 000)	9	$f^{4}dsp$	a
Po	527	9	(24.1)		(3000)	9	31 244		9	$s^{2}p^{4}$	a
Pr	1205	6	21.25	16	1646	6	80 762	(132 460)	6	$f^{2}dsp$	
Pt	2045	6	10.32	16	5380	23	126 671	(200 590)	6	$d^{7.5}sp^{1.5}$	
Pu	913	6	14.53	16	680	6	79 290	130 390	6	$d^{1.5}sp^{0.5}$	
Ra	973	9	(44.8)		(2000)	9	33 858	72 160	9	$d^{0.5}sp^{0.5}$	a
Rb	312.63	6	58.42	16	524	6	18 768		6	s	
Re	3459	6	(9.96)	16	(7942)	6	169 117	223 320	6	$d^{5}sp$	
Rh	2236	6	(9.27)	16	6321	24	123 103	234 600	6	$d^{6.5}sp^{1.5}$	
Rn	(202)	6	(50.5)		(690)	6	3570		6	$s^{2}p^{6}$	b
Ru	2527	6	(9.27)	16	(5803)	6	146 978	196 580	6	$d^{6.3}sp^{0.7}$	
S	388.37	6	(17.69)		410.5	6	65 781		6	$s^{2}p^{4}$	
Sb	903.89	6	20.03	16	4750	6	57 776		6	$s^{2}p^{3}$	
Si	1814	6	(15.0)		3369	6	81 588	120 490	6	$d^{1.5}sp^{0.5}$	a
Se	494	6	19.86	16	1473	25	50 281		6	$s^{2}p^{4}$	
Si	1687	6	11.13	16	12 082	6	94 063	189 360	6	sp^{3}	
Sm	1346	6	(21.66)		2060	6	43 655	(127 660)	6	$f^{5}dsp$	a
Sn	505.118	6	17.02	16	1680	6	70 033	183 330	6	sp^{3}	
Sr	1042	6	36.97	21	(2200)	9	35 056	81 460	9	$d^{0.5}sp^{0.5}$	
Ta	3293	6	(12.06)	16	(7560)	6	178 965	217 770	6	$d^{3.5}sp^{0.5}$	
Tb	1632	6	(20.57)		2580	6	86 205	(128 810)	6	$f^{8}dsp$	a
Tc	2477	6	(9.6)		(5668)	6	144 200	179 200	9	$d^{5.3}sp^{0.7}$	a
Te	722.66	6	21.93	16	4180	6	46 247		6	$s^{2}p^{4}$	
Th	2031	6	(21.8)	21	(3653)	6	134 374		6		a

cont'd.

Table I, contd.

Ti	1946	6	11.57	16	3580	23	104 305	136 410	6	$d^{2.5}sp^{0.5}$	
Tl	577	6	18.21	16	990	6	41 634		6	s^2p	
Tm	1820	6	(20.35)		4025	6	47 501	131 300	6	$f^{12}dsp$	a
U	1406	6	13.78	16	2204	26	120 535		6		
V	2202	6	9.50	16	4340	23	114 607	141 010	6	$d^{3.5}sp^{0.5}$	
W	3695	15	(10.51)	16	8460	23	198 996	230 900	6	$d^{4.5}sp^{0.5}$	
Xe	161.37	6	44.03	17	549	6	3079		6	s^2p^6	b
Y	1801	6	(21.1)		2724	6	93 727	130 730	6	$d^{1.5}sp^{0.5}$	a
Yb	1098	6	27.50	17	1830	6	32 764	75 460	6	$f^{14}sp$	
Zn	692.73	6	9.98	16	1750	6	28 800	121 160	6	sp	
Zr	2128	6	15.92	22	3500	23	138 470	160 870	6	$d^{2.7}sp^{0.3}$	

a = See appendix

b = Triple point

c = 35.5 atm

d = 103 atm

e = normal boiling point, volume strongly influenced by quantum effects

f = ΔH_f re-calculated using additional references[6]

g = 43 atm

Appendix

Methods of estimation of experimentally undetermined quantities, or quantities not already estimated in the references, are explained in this appendix. Metallic radii are from Zachariasen.[27]

Ac - The volume was calculated using Zachariasen's preferred metallic radius. The multiplication factor to account for thermal expansion and phase change was 1.04, in analogy with La.

Am - Zachariasen's radius for the hexagonal phase was used. The multiplication factor was 1.05, in analogy with Sm and Gd. The heat content values of Gd^6 were used in the absence of data for Am.

At - The volume was obtained by extrapolation of values for elements of the same group.

Bk - The volume was estimated as for Am, using a multiplication factor of 1.07 derived from Tb. Heat content values for Tb^6 were used.

Cf - The metallic radii of the hexagonal phases of Am and Bk were linearly extrapolated for the elements beyond Bk in their $f^{n-1}dsp$ configurations. The radius of Gd is slightly higher than would be predicted from the other $f^{n-1}dsp$ lanthanides. The radius of Cm is correspondingly higher than those of Am and Bk, and has not been used in the extrapolation. The multiplication factor for Cf was 1.09, derived from Dy. The observed melting point of 1173 K[3] was probably not Cf metal.[4] Heat content values of Dy^6 were used.

Cm - The volume was estimated as for Am, with a multiplication factor of 1.05, derived from Gd. Heat content values of Gd^6 were used.

Dy - The volume was estimated from values for the solid,[2] thermal expansion,[28] and phase change.[29]

Er - The volume was estimated as for Dy.

Es - The volume was estimated as for Cf, with a multiplication factor derived from Ho of 1.12. Heat content values of Gd^6 were used.

cont'd.

App., contd.

Eu - The volume was estimated as for Dy.

Fm - The volume was estimated as for Cf, with a multiplication factor derived from Er of 1.14. Heat content values of Gd^6 were used.

Fr - The volume was estimated as for Ac, with a multiplication factor derived from Cs of 1.02.

Gd - The volume was estimated as for Dy.

Ho - The volume was estimated as for Dy.

Lr - The volume was estimated as for Cf, with a multiplication factor derived from Lu of 1.10. Heat content values of Tm^6 were used.

Lu - The volume was estimated as for Dy.

Md - The trivalent metallic radius was estimated as for Cf, and 0.238 Å, derived from the excess radii of divalent Eu and Yb over the trivalent lanthanides, was added to predict the divalent radii. The multiplication factor derived from Yb was 1.11. Heat content values of Yb^6 were used.

No - The volume and heat content values were estimated as for Md.

Np - Volume estimated from volume of solid at 600 K and multiplication factor of 1.08.

Pa - The volume was estimated as for Ac, with a multiplication factor of 1.1 derived from U.

Pm - The volume was estimated as for Dy. The effect of phase change was estimated.

Po - The volume was estimated by extrapolation of the values for elements of the same group.

Ra - The volume was estimated as for Ac, with a multiplication factor of 1.09 derived from Ba.

Rn - The volume was estimated by extrapolation based on trends in the neighboring groups.

cont'd.

App., contd.

Sc - The volume was estimated as for Dy. The effect of phase change was estimated.

Sm - The volume was estimated as for Dy.

Tb - The volume was estimated as for Dy.

Tc - The volume was estimated by interpolation among elements of the same period.

Tm - The volume was estimated as for Dy.

Y - The volume was estimated as for Dy. The effect of phase change was estimated.

References

(1) L. Brewer, The Cohesive Energies of the Elements, LBL Report 3720 (1975).

(2) J. Donohue, The Structures of the Elements, Wiley and Sons, New York (1974).

(3) R. G. Haire and R. D. Baybary, J. Inorg. Nucl. Chem., 36, 1295 (1974).

(4) J. M. Fournier, J. Phys. Chem. Solids, 37, 235 (1976).

(5) W. H. Zachariasen, J. Inorg. Nucl. Chem., 37, 1441 (1975).

(6) R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley and D. D. Wagman, "Selected Values of the Thermodynamic Properties of the Elements," American Society for Metals, Metals Park, Ohio (1973).

(7) D. R. Stephens, H. D. Stromberg and E. M. Lilley, J. Phys. Chem. Solids, 29, 815 (1968).

(8) E. H. Baker, Inst. Min. Metall., Trans., Sec. C, 83, C237 (1974).

(9) D. R. Stull and G. C. Sinke, Advances in Chem. Ser., No. 18 (1956).

(10) C. E. Holcombe, Jr., D. D. Smith, J. D. Lore, W. K. Duerksen and D. A. Carpenter, High Temp. Sci., 5, 349 (1973).

(11) H. R. Leider, O. H. Krikorian and D. A. Young, Carbon, 11, 555 (1973).

(12) J. W. Ward, R. W. Ohse and R. Reul, J. Chem. Phys., 62, 2366 (1975).

(13) A. Cezairliyan, High Temp.-High Press., 4, 453 (1972).

(14) W. Müller, Chemiker-Zeitung, 97, 531 (1973).

(15) A. Cezairliyan, High Temp. Sci., 4, 248 (1972).

(16) A. F. Crawley, Int. Met. Rev., 19, 32 (1974).

(17) L. J. Wittenberg and R. DeWitt, J. Chem. Phys., 56, 4526 (1974).

(18) International Critical Tables, E. W. Washburn, Ed., McGraw-Hill, New York, 3, 20 (1926).

(19) Landolt-Börnstein, "Zahlenwerte und Funktionen," 6th Ed., Bd. II: 1, Spinger-Verlag, Berlin-Heidelberg, 1971.

(20) W. Klemm, H. Spitzer and H. Niermann, Angew. Chem., 72, 985 (1963).

(21) D. J. Steinberg, Met. Trans., 5, 1341 (1974).

(22) V. V. Sumin and Sh. I. Peizulaev, Russ. J. Phys. Chem., 47, 910 (1973).

(23) D. W. Bonnell, Ph.D. Thesis, Rice University, 1972.

(24) A. I. Savvatinskii, Teplofiz. Vys. Temp., 11, 1187 (1973).

cont'd.

Ref., contd.

(25) F. Grønvold, J. Chem. Thermodyn., 5, 525 (1973).

(26) H. Stephens, private communication to L. Brewer, 1974.

(27) W. H. Zachariasen, J. Inorg. Nucl. Chem., 35, 3487 (1973).

(28) F. H. Spedding and A. H. Daane, The Rare Earths, Wiley and Sons, New York, 1961.

(29) A. Jayaraman, Phys. Rev., 139A, 690 (1965).